Gas Standards Based on Optical Spectroscopies

NIST is developing frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) technologies to enable higher quality gas standards. New applications for gas standards demand high-precision measurements of low concentrations of reactive and nonreactive gases. This challenge requires developing new generation standards linked to intrinsic molecular properties. We plan to realize and disseminate new primary gas standards using quantitative absorption spectroscopy. This work is relevant to emissions of toxic industrial compounds and emissions from ground and air transportation systems, air pollution monitoring (US Environmental Protection Agency), metrology of high-purity gases for semiconductor and photonics manufacturing, terrestrial and extraterrestrial atmospheric science (National Aeronautics and Space Administration), defense (Department of Defense and Department of Energy), health care diagnostics and homeland security (Department of Homeland Security).

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NIST is developing new primary gas standards using quantitative absorption spectroscopy. In order to accomplish this, we are combining: (1) frequency-stabilized cavity ring-down spectroscopy (FS-CRDS), (2) low-uncertainty methods of sample preparation and, (3) absolute measurements of absorption line intensities for low-molecular-mass target analytes; e.g., small hydrocarbons, H_2O, O_2 and NH_3. The advantages of CRDS as a primary measurement technique include: compact sample volumes, low uncertainty, high spectral resolution, and high sensitivity.

The goal of this program is to shift the principal realization of traceable gas measurement from consumable artifacts to intrinsic standards. For certain molecules, particularly reactive gases, recent and anticipated advances in spectroscopic measurements will make robust intensity measurements viable for quantitative gas metrology. We anticipate an accuracy rivaling and potentially surpassing traditional measurements using artifact standards.

The realization of intrinsic gas standards based on quantitative absorption spectroscopy will extend NIST capabilities in gas standards and support innovation in a variety of applications from health care to manufacturing.

During 2006 we used frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) to make low-uncertainty measurements of water vapor line intensities for a number of important rovibrational transitions in the near-infrared spectral region. These experiments were built upon our previous high-resolution H_2O line shape measurements which had shown that oversimplified models of line shapes lead to systematic errors in the determination of line intensity and number density. We also demonstrated that FS-CRDS can be used to resolve and deconvolute line blending effects that occur for overlapping and closely spaced transitions. We measured line intensities and relative line positions for blended spectra of H_2O, achieving a relative precision of 0.3% for FS-CRDS measurements of line intensity. We completed an uncertainty analysis indicating a combined relative uncertainty of 0.6% for line intensity determination; a value limited by the accuracy of the transfer standard hygrometer used for water vapor concentration measurements.

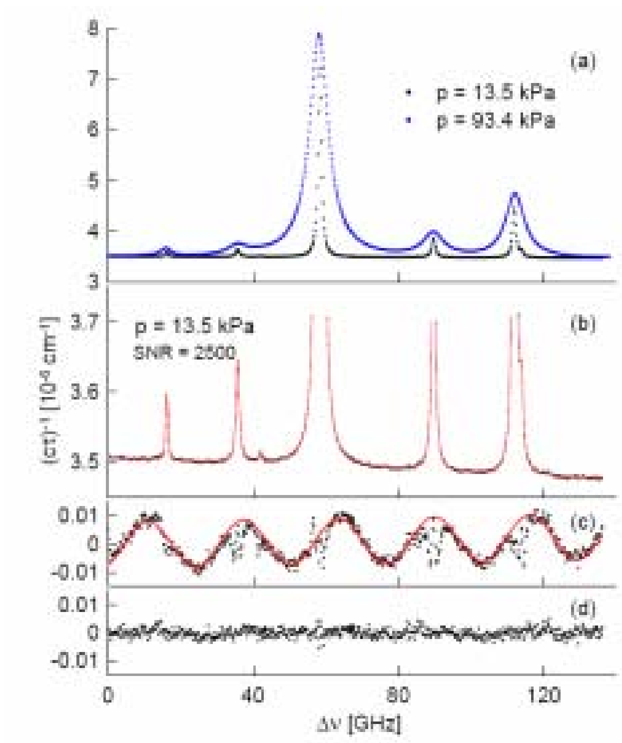

Figure. ***FS-CRDS absorption spectrum of H_2O absorption near λ = 1.39 μm. (a) measurements. (b) expanded view with Galatry line shape fits to measurements. (c) residual etaloning structure (symbols) and sinusoidal fit (line). (d) fit residuals after removing etaloning structure. The fiber-coupled DFB probe laser is shown in the inset.***

An initial study comparing FS-CRDS measurements against NIST CH_4-in-air standard reference materials, ranging from 1 µmolmol^{-1} to 100 µmolmol^{-1} was also completed. The FS-CRDS measurements probed four closely spaced $2\nu_3$ transitions at approximately 6057.0 cm^{-1}. Current results demonstrate that the long-term precision of the FS-CRDS measurements are comparable to the uncertainties of the gravimetrically prepared standards. It is important to note that the quality of the results is highly dependent upon the data analysis methods. Using a Galatry line shape model, which accounts for both the collisional narrowing and the pressure broadening of the line profile significantly improves the results compared to the results obtained using simpler line shape models. Additionally, this work produced line intensity values linked to NIST primary gravimetric standards, which can be applied in future measurements to value assign an unknown sample.

We also completed an automated and mobile FS-CRDS apparatus, which uses fiber-optic coupled distributed-feedback laser technology, with broader application to other NIST projects involving trace water vapor for humidity standards and atomic-layer film deposition processes. We used this system to measure trace water vapor concentration in ultra-dry streams of N_2. ***Figure 1*** shows a survey spectrum obtained with this apparatus corresponding to an H_2O molar fraction of 4.3 nmol mol^{-1}. We linked FSCRDS measurements to thermodynamic-based primary humidity standards maintained at NIST, achieving a detection limit of better than 0.7 nmol mol^{-1}.

Impact: The realization of intrinsic gas standards based on quantitative absorption spectroscopy will extend NIST capabilities in gas standards to lower concentrations, to reactive species that are unsuitable for long-term storage in cylinders, and to trace impurities in bulk process gases. Additional advantages to customers include: lower uncertainties, coverage of new species, potentially lower cost for standard mixtures, more flexibility in terms of dilution gas(es), and the availability of low-uncertainty molecular property data universally applicable to spectroscopic measurements of gas concentration. Customers include current and new consumers of NIST standard gas mixtures, and users of molecular spectroscopy line intensity data.

Future Plans: During 2007, we will use FS-CRDS to measure infrared spectral line shapes and line intensities of H_2O (1.38 µm band), CH_4 (1.65 µm band) and O_2 (A-band near 0.76 µm). The portable FSCRDS spectrometer will be coupled directly to NIST primary humidity standards and comparisons with commercial CRDS systems will be implemented. Additionally, we are extending these ultra-sensitive cavity-enhanced capabilities to directly address the DoD/DHS calibration and validation needs of deployed and to-be-deployed chemical detectors.

Publications:

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P.M. Chu, J.T. Hodges, G.C. Rhoderick, D. Lisak, J.C. Travis, **"Methane-in-Air standards measured using a 1.65 m frequency-stabilized cavity ring-down spectrometer,"** in Chemical and Biological Sensors for Industrial and Environmental Monitoring, Proc. SPIE , Oct. 2006.

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